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HYDRATION AND MICROSTRUCTURAL PROPERTIES OF CEMENT PASTE CONTAINING NANO AND MICROSILICA

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The influence of nano- and microsilica addition on ordinary Portland cement (OPC) pastes has been studied in terms of hydration and microstructural properties. Three different combinations of nano- and microsilica mixes were used. A constant water-binder ratio of 0.35 was maintained throughout the experiment. All samples were tested for initial and final setting time and compressive strengths were determined at the age of 3, 7, 28, and 90 days of hydration. The hydration products were examined by SDT and XRD analysis at various curing ages. The inclusion of nano- and microsilica reduced the initial and final setting time significantly, increased the compressive strength of hardened cement paste after 7 days of hydration, and reduced the amount of calcium hydroxide in the hardened paste compared to mixes without these nanoparticles.

Keywords: Microstructures, Strength, Electron microscopy, Thermal analysis.

1 INTRODUCTION

Microsilica, commonly known as silica fume (SF), is a by-product of silicon metal or ferrosilicon alloys in the manufacturing process (Siddique and Chahal 2011). Microsilica particles consist essentially of fine silica in non-crystalline form, approximately one-hundredth the size of a cement particle, thus possessing a high specific surface area and chemically exhibiting great pozzolanic reactivity (Ganesh Babu and Surya Prakash 1995). The pozzolanic reaction in the chemical phase consumes and subsequently transforms the weak calcium hydroxide (CH) into strong calcium-silicate-hydrate gel (C-S-H) (Rao 2003, Temiz and Karakeci 2002, Yajun and Cahyadi 2003). Microsilica also has a physical phase which refines the void system of the cement paste and the interfacial zone. However, some studies have shown that the activity of microsilica at early ages is low (Larbi et al. 1990, Mitchell et al. 1998).

Much research has been done on understanding the effects of nanosilica (NS) on the properties of cement paste (Jo et al. 2007, Najigivi et al. 2013, Senff et al. 2010, Stefanidou and Papayianni 2012). NS have been used either to substitute part of cement or as an admixture in cement pastes. In the fresh state, an improvement of rheological properties has been recorded, while in the hardened state, the compressive strength was enhanced. According to Sobolev et al. (2009), the changes recorded in modified mixes with NS particles are due to the chemical reaction between silica oxide and calcium hydroxide (CH), released during cement hydration, and also due to physical modifications such as compaction improvement as a result of pore refinement. Both mechanisms indicate that the addition of NS is contributing to an increase of strength and permeability reduction of the hardened cement paste.

2 EXPERIMENTAL PROGRAM

2.1 Materials

Commercial Swan General-Purpose Portland Cement (Type GP) was used. Both NS and SF in this study were undensified materials. The chemical compositions of the raw materials used are summarized in Table 1.

Table 1. Chemical compositions and physical properties of OPC, SF, and NS.

Materials	Chemical composition (%)						Physical properties	
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Specific surface (m^2/g)	Density (g/cm^3)
OPC	21.1	4.7	2.7	63.3	2.6	2.5	0.4	2.9
SF	97.8	-	-	-	-	0.3	21.5	2.2
NS	100	-	-	-	-	-	160	2.1

2.2 Mix Design and Casting of Specimens

Cement pastes with combinations summarized in Table 2 were mixed and cast using a Hobart Mixer according to ASTM C305-12. The fresh pastes were cast into 50 mm cube molds and compacted on a vibrating table. The samples were cured in water storage tanks at temperature 23ºC ±2ºC until the time of testing. The curing water was saturated with calcium hydroxide to prevent leaching of CH from the specimens.

Table 2. Mix proportions.

Mix Details	OPC (%)	SF (%)	NS (%)	W/B
Mix 1 (OPC100)	100	0	0	0.35
Mix 2 (OPC90SF10)	90	10.0	0	0.35
Mix 3 (OPC90SF8.5NS1.5)	90	8.5	1.5	0.35

2.3 Test Methods

Periodic penetration tests were performed on the cement paste by Vicat apparatus to determine the initial and final setting time, as per ASTM C191-08 requirement (ASTM International 2008). Three cubes from each mixes were tested as per ASTM C109M-11 (ASTM International 2011) at 3, 7, 28, and 90 days, to determine the compressive strength of the specimens. The microstructural properties were analyzed by means of SDT and XRD.

SDT testing is the simultaneous testing of a sample with Differential-Thermal Analysis (DTA) and Thermo-Gravimetric Analysis (TGA). The TGA test is used to quantify the chemical phases present in the sample by determining the amount of mass lost within a certain temperature range. In the case of CH, the decomposition of the phase is reported (Vedalakshmi et al. 2003) to be between the temperature ranges of 400ºC to 510ºC, whereby the mass loss is attributed to the loss of water from the CH phase. A simple equation can be used to estimate the CH percentage within the samples as follows:

$$\text{Percentage of CH} = \frac{\text{Molecular mass of CH}}{\text{Molecular mass of water}} \times \%\,\text{loss of water mass} \qquad (1)$$

X-Ray Diffraction (XRD) is a technique used to determine the mineral properties of a crystalline solid. When a crystalline solid is exposed to X-Rays of a particular wavelength, layers of atoms diffract and produce a pattern of peaks, which characterise the minerals present in the material.

3 RESULTS AND DISCUSSION

3.1 Setting Time of the Cement Paste

The effects of NS and SF on the setting time of cement paste are shown in Figure 1. It was observed that the initial and final setting times of cement paste containing SF and NS are less than the control mix. Also, the initial setting times of cement paste containing NS are less than the cement paste without NS. The pozzolanic reaction of SF and NS seems to be very active at the early hours of hydration, especially for mixes with the addition of NS. As a result, there was a significant shortening of initial and final setting times of the pastes as compared to the control sample. The reduction of the setting times of the NS cement paste may be related to the finer particle size and higher surface area of the NS, compared with those of SF which reduced the dormant period and increased the cement hydration. This is in agreement with the findings of Rao (2003), who reported that SF results in quick setting of cement. Qing et al. (2007) have also observed similar results.

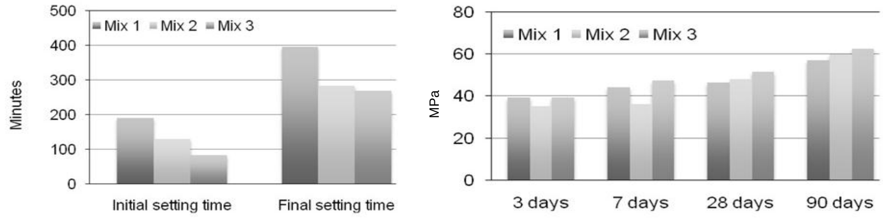

Figure 1. Setting times, compressive strength of cement paste containing SF and NS.

3.2 Compressive Strength

The effects of SF and NS on the compressive-strength development of the cement paste are shown in Figure 1. It can be seen that the strength of cement paste containing 10% SF was less than the control up to 7 days. However, the strength was more than the control both at 28 and 90 days. On the other hand, for the mix containing NS, the strength at 3 days was close to that of the control, but eventually exceeded the control mix at 7, 28, and 90 days.

Both NS and SF are nano-sized highly-reactive silica, but the average primary particle size of NS is about 10 times smaller than that of SF. As such, the physical and chemical effect of NS is likely to be more substantial than the SF. From a physical perspective, the extremely fine particle size of the NS may have accelerated cement hydration by providing a high amount of nucleation sites for the precipitation of cement hydration products. The accelerated cement hydration may also result in an increased amount of CH in solution, which may activate and speed up the development of CSH. In addition to the nucleation effect, NS may have acted as a reactive filler, which reduces bleeding and increases packing density of the paste by occupying space between the cement and SF particles, hence contributing to the increased early strength. From a chemical point of view, the highly-reactive pozzolanic NS reacts with CH from cement hydration to form calcium silicate hydrate (CSH).

3.3 Analysis of Hydration Products Using SDT

The results of SDT tests for mix 1 at 3 days are shown in Figure 2. The DTA curves of all samples exhibited a similar trend. There are three obvious dips in the curve, which are located approximately at 100ºC, 480ºC, and 700ºC. These dips are associated with the decomposition of ettringite, CSH gel, CH, and $CaCO_3$ respectively.

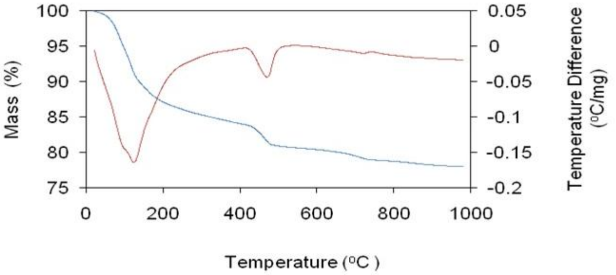

Figure 2. SDT analysis for Mix1 at 3 days.

Table 3. Estimated percentage of CH.

Days	Mix 1	Mix 2	Mix 3
3	13.00	10.90	10.63
7	13.72	11.47	10.69
28	15.21	12.85	11.62

The basis for determining the CH content within the sample as mentioned earlier was used to determine the estimated percentage of CH. These steps were repeated for the remaining samples to produce the numbers as shown in Table 3. The result in Table 3 shows that CH increases with age. Regardless of the mix type, the inclusion of SF and NS in cement paste reduces the amount of CH when compared to the control mix, due to the pozzolanic reaction of the nanoparticles with CH to develop more CSH.

3.4 Mineralogical Analysis of Hydration Products Using XRD

The XRD patterns of the hydration products of the mixes are shown in Figure 3. The presence of calcium carbonate was attributed to the partial carbonation of portlandite. After 28 days of hydration of the control mix, the intensity of ettringite main peaks reduced significantly; this may attributed to the transformation of calcium sulphoaluminate to a more stable form of calcium aluminate hydrate. A considerable increase in amount of CH is also observed, mainly due to an increase in formation of C-S-H products. In the case of SF- and NS-added samples, e.g., mix 2 and mix 3, one can easily observe that after 28 days of curing, the amount of crystalline CH seems to be reduced. This is indicated by the shorter length of CH peaks compared to the 3-day samples. This again showed evidence of a pozzolanic reaction of SF or NS with the CH to form more CSH matrixes.

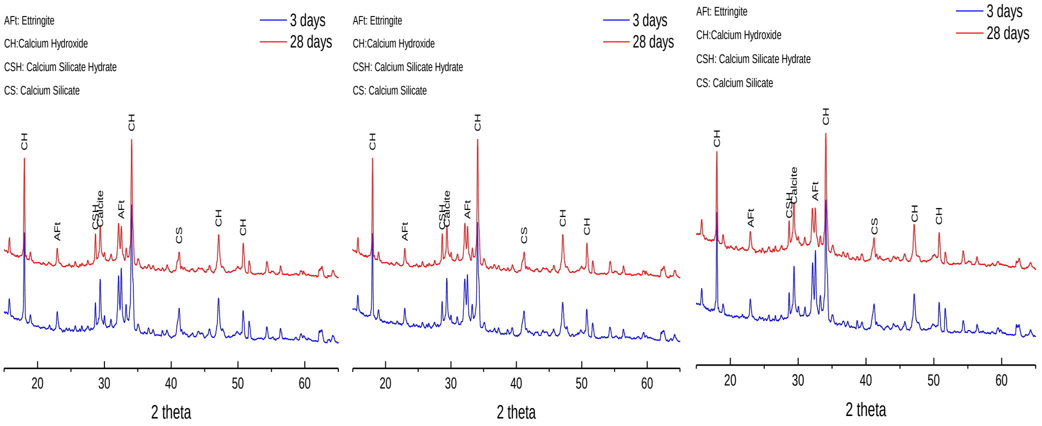

Figure 3. XRD patterns of Mix 1, 2 and 3 hydration products at age of 3 and 28 days.

4 CONCLUSIONS

(1) Both NS and SF reduced the initial and final setting time significantly, as compared to mix without these nanoparticles.

(2) The addition of NS and SF increases the compressive strength of hardened cement paste after 7 days of hydration. It seems that mix with the addition of NS enhances an early rate of hydration more rapidly than the mix with SF.

(3) The analysis using SDT confirmed that the overall percentage of hydration products (CSH and CH) increases with the age of hydration regardless of the mix type. On the other hand, the inclusion of SF and NS in the mix reduces the amount of CH in the hardened paste, as compared to the mix without these substitutions.

(4) The XRD analysis showed that CSH and CH of the control mix continued to increase with the age as a result of the continuation of hydration until 28 days of curing age. Also, there was significance decrease in the amount of ettringite due to the transformation of calcium sulphoaluminate to calcium aluminate hydrate.

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